

Supercritical carbon dioxide extraction to produce low-*k* plasma enhanced chemical vapor deposited dielectric films

J. A. Lubguban, J. Sun,^{a)} T. Rajagopalan, B. Lahlouh, S. L. Simon,^{a)} and S. Gangopadhyay^{b)}

Nano Tech Center, Texas Tech University, Lubbock, Texas 79409

(Received 21 June 2002; accepted 3 October 2002)

A treatment to reduce the dielectric constant of plasma enhanced chemical vapor deposition (PECVD) films is presented. The method involved extracting low molecular weight or CO₂ soluble species in the films by post deposition supercritical CO₂ pressurization (SCCO₂). We observed a decrease in *k* value of about 10%–14% in a composite film of organosilicate and *a*-C:F after SCCO₂ treatment at 200 °C for 8 h. The composite films were deposited by PECVD using C₄F₈ and tetravinyltetramethylcyclotetrasiloxane (TVMCTS) liquid source and H₂ carrier gas at room temperature. As-deposited films were also annealed at 200 °C for 8 h in N₂ atmosphere to compare the effect of thermal annealing without SCCO₂ treatment. The result shows that there is no change in the *k* of the films after annealing. Thus, SCCO₂ extraction is a good method for reducing the dielectric constant of these PECVD composite films. Supercritical CO₂ pressurization of the film deposited using TVMCTS and H₂ only without the addition of C₄F₈ has no effect on the dielectric properties of the film while SCCO₂ treatment of *a*-C:F samples deposited using C₄F₈ only dissolved the film. Therefore, in the composite film, we expect that CF_x species dissolve during SCCO₂ treatment while the organosilicate structure is preserved. Analysis of the Fourier-transform infrared spectra of the samples supports this hypothesis based on the decrease in the C–F absorption intensity after SCCO₂ treatment. © 2002 American Institute of Physics.

[DOI: 10.1063/1.1525390]

The need for low-*k* films for new generation interlevel and intermetal dielectrics in ultralarge scale integration devices has led to various preparation and treatment methods.^{1,2} The spin coating technique is most promising since materials with *k* less than 2.0 can be produced.^{2,3} For example, researchers can engineer the porosity of spin-on silica through ageing to obtain a *k* value ranging from 1.1 to 4.0.^{1,2} However, there remain tough issues to be solved like shrinkage and high etch rates for cylindrical molecular pump process.² Thus, for films with *k* < 2.0, there is still no known manufacturable solution as reported by the International Technology Roadmap for Semiconductors in 2001. In this letter we present a method of reducing the dielectric constant by supercritical CO₂ pressurization (SCCO₂) of plasma enhanced chemical vapor deposition (PECVD) films.

The goal of this method is to create nanopores in the films by extracting unbonded and loosely bonded low molecular weight and CO₂ soluble species by SCCO₂ treatment. This is similar to removing CH_x in dual phased SiCOH and organic film through thermal annealing, thus creating voids and, hence, low *k*.⁴ At temperatures and pressures greater than 31 °C and 1050 psi, respectively, CO₂ becomes supercritical and acts like a liquid solvent. The solvent-like property of SCCO₂ with a mixture of cosolvent has been used by Los Alamos National Laboratory to successfully remove photoresist and it produced virtually no hazardous wastes.⁵ Several groups of researchers have studied the solubility of polymers in SCCO₂.^{6–11} High molecular weight species are

generally insoluble in CO₂ unless there are strong specific interactions between the CO₂ and the polymer. For example, high molecular weight perfluoropolymers,¹² hydrofluorocarbon polymers,¹³ and chlorofluorocarbon polymers¹¹ have been found to be soluble in CO₂. On the other hand, oligomers and low molecular weight compounds are often soluble, especially those containing CO₂-philic groups, such as siloxanes and perfluoro groups.¹⁴ We have performed studies of the effect of SCCO₂ treatment on PECVD deposited fluorocarbon (*a*-C:F) films using C₄F₈ gas. The films dissolved in SCCO₂.

In a previous article,¹⁵ we investigated low-*k* organosilicate films using a liquid source, tetravinyltetramethylcyclotetrasiloxane (TVMCTS). This source has an open structure and we have succeeded in preserving the ring structure after plasma polymerization using PECVD. The result is a film with a relatively low density and *k* of 2.65 to 2.92 and thermal stability up to 400 °C. More importantly, these films were stable after CO₂ pressurization up to 9000 psi and pressurization temperatures up to 200 °C. These stable properties make this film a good matrix from which CO₂ soluble species can be extracted. The methodology of the present study is as follows; A composite film is deposited mainly of TVMCTS organosilicate film and of low molecular weight *a*-C:F loosely bonded or unbonded to the organosilicate main structure. Since *a*-C:F film dissolved with pressurization, we speculated that *a*-C:F incorporation and removal by SCCO₂ would create nano or molecular scale porosity without adversely affecting the mechanical integrity or thermal stability of the matrix. To facilitate this experiment, C₄F₈ gas

^{a)}Also at: Department of Chemical Engineering.

^{b)}Electronic mail: gango@ttu.edu

TABLE I. Deposition conditions.

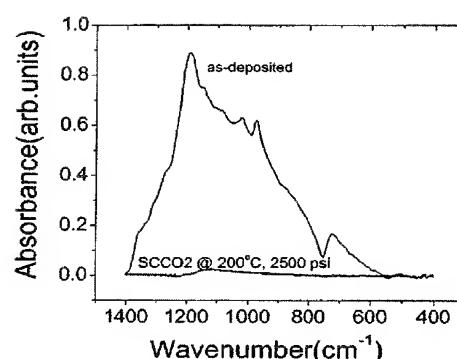
Film	TVMCTS + H ₂ (sccm)	C ₄ F ₈ (sccm)	rf power (W)	Pressure (Torr)	Temperature (°C)
1	20	20	6	0.3	25
2	20	3	3	0.3	25
3	20	0.5	10	1	25
4	20	0	3	0.3	25
5	0	40	50	0.3	25

is mixed in the TVTMCTS and H₂ plasma. The composite film is then exposed to post deposition SCCO₂ treatment.

The organosilicate and α -C:F composite films with thickness of 0.75–1.75 μm were deposited on *p*-type Si (0.008–0.02 and 40–60 Ωcm resistivities) and quartz substrates in a capacitively coupled, 13.56 MHz PECVD system. As stated earlier, we used TVTMCTS liquid source with H₂ as carrier gas to deposit the organosilicate film and added C₄F₈ gas in the plasma to fabricate a composite film. The experimental conditions for five films that will be used for analysis throughout this letter are listed in Table I. The rf power was kept as low as possible to prevent the ring structure of the TVTMCTS source from breaking since the rings provide an open structure and is the main reason for low k in the TVTMCTS films.⁴ All films were deposited at RT and the C₄F₈ flow rate was varied to obtain films with different CF_x concentrations. A film with conditions similar to film 2 but without C₄F₈ gas was also fabricated for comparison (film 4). Film 5 is an α -C:F film and was used to show the solubility of α -C:F in SCCO₂.

The SCCO₂ extraction process was performed as follows: The as-deposited films (about 2 \times 2 cm dimension) were placed inside a small cylindrical stainless steel pressure chamber with inner diameter of 2.5 cm, outer diameter of 10.2 cm, and depth of 12.7 cm. The ambient air was then pumped out for several minutes using a roughing pump. The chamber temperature was then ramped slowly to achieve the desired pressurization temperature of 200 °C. The chamber was subsequently pressurized isothermally with CO₂ (99.99%) using a gas booster pump (Haskel) driven by air at 70 psi. The pressure of the chamber was then maintained at 8650 psi for 8 h. After the extraction was completed, the vessel was depressurized to 500 psi and the temperature was ramped down to RT. Depressurization was completed at RT.

In addition to the SCCO₂ extraction studies, we compared SCCO₂ treated and thermally annealed films. Anneal-

FIG. 1. FTIR spectra of as-deposited and SCCO₂ α -C:F film.

ing without SCCO₂ was done in a vacuum chamber in N₂ atmosphere for 8 h at 600 mTorr.

Measurements of Fourier-transform infrared spectroscopy (FTIR), thickness, and k were performed for as-deposited and SCCO₂ treated samples. The FTIR spectra were measured using a Perkin-Elmer model 1600 spectrometer. The capacitance of the film was measured at 10 kHz.

Table II shows the effect of SCCO₂ treatment on the thickness and dielectric constant for films 1–4 listed in Table I. The dielectric constants of the composite films after CO₂ extraction at 8650 psi at 200 °C for 8 h were reduced by 10%–14%. As a comparison, when the films (fresh set of films 1–4) were only annealed at 200 °C for 8 h in N₂, we observed no significant change in either k or thickness. However, the k and thickness of film 4 deposited without C₄F₈ were unchanged in both treatments. Thus, the supercritical CO₂ pressurization treatment is a good method to reduce the k value of the composite films.

The ability of SCCO₂ to dissolve α -C:F films is demonstrated by comparing the FTIR spectra of an α -C:F film (film 5 in Table I), as-deposited and after subsequent SCCO₂ treatment as shown in Fig. 1. The broad absorption band from 400 to 1400 cm⁻¹ is typical of a soft, highly disordered, and low crosslinked α -C:F polymer film. After the film was pressurized at 2500 psi and 200 °C for 10 h, the C–F absorption band intensity is almost negligible as seen in Fig. 1. Initially, the as-deposited film had a thickness of about 1 μm and it decreased significantly after SCCO₂. Thus, SCCO₂ dissolved the α -C:F film. However, α -C:F films deposited with the same conditions but at higher temperatures did not dissolve in SCCO₂ presumably because of higher crosslinking density. The addition of gases like H₂ in C₄F₈ during deposition also produced a highly crosslinked α -C:F films that have higher resistance to SCCO₂ treatment.

The FTIR spectra of organosilicate films deposited with and without C₄F₈ incorporation (films 2 and 4) are shown in Fig. 2. We have attributed in detail the absorption bands of the organosilicate film without C₄F₈ in a previous article.¹⁵ In summary, the broadband around 945–1220 cm⁻¹ consists of Si–O in linear (1010 cm⁻¹) and ring (1065 cm⁻¹) configurations. Other bands present are Si–O_{bend} (790 cm⁻¹), Si–CH₃ (1265 cm⁻¹), and CII group (2800–3000 cm⁻¹). The addition of fluorocarbon in the film gives rise to a Si–F band centered at 900 cm⁻¹. In addition, the band around 945–1220 cm⁻¹ attributed to Si–O in the TVTMCTS spectrum becomes broad and extended to the frequency range of

TABLE II. Effect of SCCO₂ at 8650 psi, 200 °C, 8 h.

Film	Thickness (μm)	k	Treatment
1	1.7441 ± 0.021	2.87 ± 0.10	As-deposited
	1.5194 ± 0.019	2.48 ± 0.09 (14.0% decrease)	SCCO ₂
2	0.7533 ± 0.015	3.82 ± 0.14	As-deposited
	0.7285 ± 0.010	3.34 ± 0.09 (12.5% decrease)	SCCO ₂
3	0.7543 ± 0.007	3.42 ± 0.10	As-deposited
	0.6791 ± 0.018	3.07 ± 0.09 (10.2% decrease)	SCCO ₂
4	1.1860 ± 0.0148	2.71 ± 0.05	As-deposited
	1.1860 ± 0.0148	2.71 ± 0.05 (Unchanged)	SCCO ₂

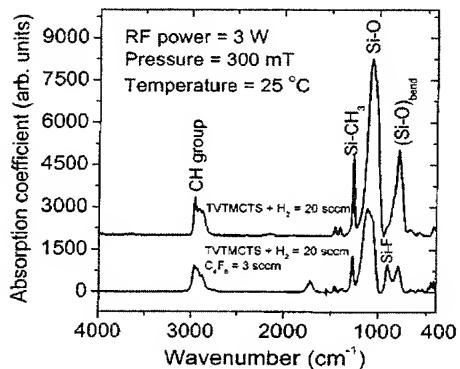


FIG. 2. Comparison of as-deposited organosilicate and composite film spectra.

1250 cm^{-1} . In fact the FWHM of this band increased from 395 to 474 cm^{-1} . Comparing Figs. 1 and 2, the Si–O absorption band for the TVTMCTS film observed at 945–1220 cm^{-1} is found to overlap with the C–F bands for α -C:F film at 600–1400 cm^{-1} (Fig. 1). Thus, the increase in full width at half maximum of the Si–O band for the composite film is due to additional C–F bands along with the Si–O (linear) and Si–O (ring) bonds at the high wave number side. As can be observed from Fig. 2, it is clear that the Si–O and Si–CH₃ absorption intensities were reduced significantly with C₄F₈ addition. Further inspection shows that the CH group also reduced. Thus, incorporation of CF species adversely affects the robust structure of the organosilicate films by breaking Si–O (rings and chains) and replacing O and CH₃ bonded to Si with F. Breaking of Si–O rings and lower Si–CH₃ bond concentration is expected to enhance the film density and, hence, increase the dielectric constants. The addition of F to the SiO₂ structure (i.e., formation of Si–F) is normally expected to decrease the dielectric constant, but the contrary is observed here. For the same deposition conditions, the addition of C₄F₈ increases the k for TVTMCTS film from 2.71 (film 4) to 3.82 (film 2). In our previous article, we claimed that the main reason for the decrease in k in the TVTMCTS organosilicate film is the open structure provided by the TVTMCTS and the robust methyl groups resulting in a less dense film.¹⁵ For the composite film studied here, we speculate that the expected decrease in k contributed by the addition of Si–F was offset by the increase in k due to the large reduction in the Si–O ring structures and Si–CH₃ concentration. However, as more C₄F₈ is added in the case of film 1 the dielectric constant reduces. This is because the composite film now consists mostly of α -C:F with some organosilicate incorporation. A pure α -C:F film can have a dielectric constant as low as 2.3.¹⁶ The spectra of this film shows that indeed the C–F absorption intensity is more dominant than Si–O and Si–CH₃ bands.

The change in the FTIR spectra at 950–1250 cm^{-1} range before and after SCCO₂ treatment of film 2 is shown in Fig. 3. The SCCO₂ treatment of the film clearly decreases the intensity of the band especially in the higher wave number side corresponding to the C–F absorption band. Thus, we conclude that low molecular weight C–F bonds dissolved in SCCO₂. The dissolution of the C–F bonds is expected to

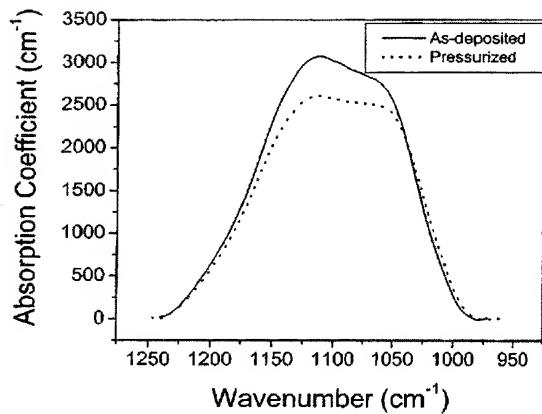


FIG. 3. Changes in the absorption intensity of 950–1250 band after SCCO₂ pressurization.

create molecular voids and/or nanopores in the matrix resulting in the 10%–14% decrease in k . Furthermore, our studies establish that SCCO₂ treatment is a very effective process to reduce the dielectric constant of an organosilicate film. It is important to note that all the films contain significant percent of highly crosslinked α -C:F bands after SCCO₂ treatment and only low molecular weight C–F bands with low crosslink density are dissolved.

We have presented a method that reduces the dielectric constant of PECVD deposited composite films by post deposition supercritical CO₂ pressurization. Low molecular weight species like CF or larger CO₂-soluble species containing CF_x moieties can be extracted during the process. It is hypothesized that the extraction creates molecular or nanoscale porosity thereby reducing k . For example the k decreased from 2.87 to 2.48 with SCCO₂ extraction at 200 °C. Thermal annealing in N₂ at 200 °C of the film deposited with the same conditions showed no change in k .

This research was funded by SRC, State of Texas ATP program, and the National Science Foundation.

- ¹MRS Bull. **22**, No. 10 (1997).
- ²R. Zorich, "Advance Technology Report: Copper Interconnect and Low- k Dielectric Technologies," Integrated Circuit Engineering.
- ³The International Technology Roadmap For Semiconductors, 2001.
- ⁴A. Grill and V. Patel, Appl. Phys. Lett. **79**, 803 (2001).
- ⁵Dateline Los Alamos, Fall 2001
- ⁶W. H. Tuminello, G. T. Dee, and M. A. McHugh, Macromolecules **28**, 1506 (1995).
- ⁷A. V. Yazdi, C. Lepilleur, E. J. Singley, F. A. Adamsky, R. M. Enick, and E. J. Beckman, Fluid Phase Equilib. **117**, 297 (1996).
- ⁸M. A. McHugh, *The 4th International Symp. On Supercritical Fluids*, 11–14, May 1997, Sendai, Japan.
- ⁹W. H. Tuminello, G. T. Dee, and M. A. McHugh, Macromolecules **28**, 1506 (1995).
- ¹⁰J. M. DeSimone, Z. Gaun, and C. S. Elsbernd, Science **257**, 945 (1992).
- ¹¹M. McHugh, and J. Krukonis, *Supercritical Fluid Extraction-Principles and Practice* (Butterworths, Boston, 1986), Chap. 9.
- ¹²W. H. Tuminello, G. T. Dee, and M. A. McHugh, Macromolecules **28**, 1506 (1995).
- ¹³J. M. DeSimone, Z. Gaun, and C. S. Elsbernd, Science **257**, 945 (1992).
- ¹⁴A. V. Yazdi, C. Lepilleur, E. J. Singley, W. Liu, F. A. Adamsky, R. M. Enick, and E. J. Beckman, Fluid Phase Equilib. **177**, 297 (1996).
- ¹⁵J. Lubguban, T. Rajagopalan, N. Mehta, B. Lahlouh, S. L. Simon, and S. Gangopadhyay, J. Appl. Phys. **92**, 1033 (2002).
- ¹⁶K. Endo and T. Tatsumi, Appl. Phys. Lett. **68**, 2864 (1996).

